Magnetic Properties of Ferrites—Cobaltites Bi$_{1-x}$La$_x$Fe$_{1-x}$Co$_x$O$_3$ (1.0 $\geq x \geq$ 0.7) with a Perovskite Structure

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Abstract—The molar magnetic susceptibility ($\chi_{mol}$) of Bi$_{1-x}$La$_x$Fe$_{1-x}$Co$_x$O$_3$ solid solutions ($x = 1.0, 0.9, 0.8, 0.7, 0.6$) with a crystal structure of rhombohedrally distorted perovskite ($R\bar{3}c$) has been investigated in the temperature range of 5–300 K in a 0.86 T magnetic field. In the temperature range where $\chi_{mol}$ depends on temperature $T$ according to the Curie—Weiss law, the resulting effective magnetic moments of Fe$^{3+}$ and Co$^{3+}$ ions ($\mu_{eff,Fe}^{3+},Co^{3+}$, $\mu_{eff,Fe}^{3+}$, and $\mu_{eff,Co}^{3+}$) have been determined for the solid solutions under study. Fe$^{3+}$ ions in the solid solutions have been found to be in the mixed intermediate spin (IS) and high spin (HS) states ($\mu_{eff,Fe}^{3+}$ is 4.26$\mu_B$ and 4.68$\mu_B$ for the temperature range of 5–100 and 150–300 K, respectively). It is shown that 8% Co$^{3+}$ ions in LaCoO$_3$ at 5–19 K are in the paramagnetic IS state and they determine to a great extent the magnetic susceptibility. It is established that only 9% and 18% Co$^{3+}$ ions in Bi$_{1-x}$La$_x$Fe$_{1-x}$Co$_x$O$_3$ solid solutions ($x = 0.9$ or 0.8) are in the paramagnetic IS state in the temperature ranges of 5–30 and 5–110 K, respectively, while the other ions are diamagnetic.

Keywords: perovskite, ferroelectrics (multiferroics), solid solution, bismuth ferrite, lanthanum cobaltite, magnetization, magnetic susceptibility, effective magnetic moment, spin states of Fe$^{3+}$ and Co$^{3+}$ ions

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INTRODUCTION

Currently, multiferroics (ferroelectrics), i.e., materials characterized by a relationship between magnetic and electric properties, are of great interest. However, many multiferroics exhibit their typical properties at low temperatures; therefore, particular attention is paid to the materials in which the critical temperature of ordering magnetic moments and electric dipoles exceeds room temperature. One of the most promising multiferroics is BiFeO$_3$ perovskite, where dipole and antiferromagnetic orderings exist up to 1100 and ~640 K, respectively [1–3]. As a result, this ferroelectric can be widely applied at room temperature. Moreover, this compound can be used to prepare various solid solutions, thus expanding its application range. The results of studying solid solutions of BiFeO$_3$–LnFeO$_3$ binary systems (Ln is a rare earth element), in which BiFeO$_3$ and LnFeO$_3$ have, respectively, rhombohedral and orthorhombically distorted perovskite structures, were reported repeatedly in the literature [3–12]. The Bi$_{1-x}$Ln$_x$FeO$_3$ solid solutions formed in these systems were found to have the crystal structure of rhombohedral distorted perovskite ($R3c$) at the degree of substitution $x$ of lanthanum ions (La$^{3+}$) and ions of other rare earth elements for Bi$^{3+}$ ions of not more than 0.2 and the orthorhombically distorted perovskite structure at a degree of substitution $x > 0.2$. In the BiFeO$_3$–LaCoO$_3$ system, both components have the crystal structure of rhombohedral distorted perovskite $R3c$ and $R\bar{3}c$, respectively. In this context, the region of the existence of Bi$_{1-x}$La$_x$Fe$_{1-x}$Co$_x$O$_3$ solid solutions with an orthorhombic structure is likely to be absent in this system. However, we established [13, 14] that in this system Bi$_{1-x}$La$_x$Fe$_{1-x}$Co$_x$O$_3$ solid solutions with a degree of substitution $0.2 \leq x \leq 0.6$ have the crystal structure of orthorhombically distorted perovskite, whereas at a degree of substitution of $x < 0.2$ and $x \geq 0.7$ solid solutions are crystallized into the rhombohedral structures $R3c$ and $R\bar{3}c$, respectively. In this paper, we report the results of studying the magnetic susceptibility, resulting effective magnetic moment of Fe$^{3+}$ and Co$^{3+}$, and their spin states in Bi$_{1-x}$La$_x$Fe$_{1-x}$Co$_x$O$_3$ solid solutions (1.0 $\geq x \geq$ 0.7) with a crystal structure of orthorhombically distorted perovskite in the temperature range of 5–300 K.
EXPERIMENTAL

Polycrystalline samples of $\text{Bi}_{1-x}\text{La}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ solid solutions ($x = 1.0, 0.9, 0.8,$ or $0.7$) were synthesized by solid-phase reactions method from $\text{Bi}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, $\text{La}_2\text{O}_3$ and $\text{Co}_3\text{O}_4$ oxides of analytic grade. Lanthanum oxide was previously calcined in air at $1000^\circ\text{C}$ for 1 h. Powders of the initial compounds at certain molar ratios were mixed and ground for 30 min in a “Pulverizette 6” planetary mill in the presence of ethanol. The obtained powder with ethanol added was pressed under 50–75 MPa into pellets 25 mm in diameter and 5–7 mm high and then annealed at $800^\circ\text{C}$ in air for 8 h. After preliminary annealing, the pellets were crushed, ground, and pressed to bars 30 ($5 \times 5$ mm$^2$ in size, which were then annealed at $1150^\circ\text{C}$ in air for 2 h. To avoid a possible (in synthesis and, especially, sintering) interaction of the pellets with the substrate material ($\text{Al}_2\text{O}_3$), the samples were spaced from the substrate by a thin buffer layer of powder of the same (as pellets) composition. The samples were slowly cooled along with the furnace from the sintering temperatures to room temperature (the cooling rate was 2–5 K min$^{-1}$).

X-ray diffraction patterns were obtained with a D8 ADVANCE diffractometer ($\text{CuK}_\alpha$ radiation). The parameters of the crystal structure of bismuth–lanthanum ferrites–cobaltites $\text{Bi}_{1-x}\text{La}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ were determined using an RTP tabular processor for X-ray diffractometry and the data from the International Centre for Diffraction Data (ICDD JCPDS).

Specific magnetization $\sigma_{sp}$ and molar magnetic susceptibility $\chi_{mol}$ of $\text{Bi}_{1-x}\text{La}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ solid solutions were measured in the 0.86 T magnetic field in the temperature range of 5–300 K by the vibrational method with a universal high-field measuring system (Cryogenic Ltd., London) at the Scientific and Practical Materials Research Centre, Belarussian Academy of Sciences.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the prepared $\text{Bi}_{1-x}\text{La}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ samples ($1.0 \geq x \geq 0.7$) (Fig. 1) showed that solid solutions with a crystal structure of rhombohedrally distorted perovskite ($R\bar{3}c$) are formed in this compositional range of the $\text{BiFe}_3\text{O}_5$–$\text{LaCo}_3\text{O}_5$ binary system. $\text{LaCo}_3\text{O}_5$ sample was single-phase (Fig. 1, diffraction pattern 1), whereas the $\text{Bi}_{0.1}\text{La}_{0.9}\text{Fe}_{0.1}\text{Co}_{0.9}\text{O}_3$, $\text{Bi}_{0.2}\text{La}_{0.8}\text{Fe}_{0.2}\text{Co}_{0.8}\text{O}_3$, and $\text{Bi}_{0.3}\text{La}_{0.7}\text{Fe}_{0.3}\text{Co}_{0.7}\text{O}_3$ samples contained a small amount of $\text{Bi}_{25}\text{Fe}_9\text{O}_{39}$ and $\text{Bi}_2\text{Fe}_3\text{O}_9$ impurity phases (Fig. 1, diffraction patterns 2–4). It was established that parameter $a$ and the unit-cell volume $V$ gradually